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Thermochemistry and Stability of Nuclear Waste Glasses

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Knowledge of Gibbs free energies of dissolution is needed for the borosilicate glasses used to store nuclear waste in order to model their alteration by aqueous solutions. In this paper, we first recall that, despite the fact that glasses are nonequilibrium substances, these data can be determined experimentally from a comprehensive set of measurements. Special attention is paid to configurational entropy, which cannot be determined by calorimetric methods, but has an important contribution to Gibbs free energies of formation. The results obtained for a series of simple and complex glasses are then presented. We finally discuss the composition dependence of the thermophysical properties of sodium borosilicates, whose practical importance is not restricted to the issue of nuclear waste storage.

1. Introduction

Since the 1970's the most common way to store the radionuclides produced either in electricity plants or for other uses has been to incorporate the waste in borosilicate glasses. To give a single example, 1500 tons of borosilicate glasses had already been prepared in France in 1998 for this purpose, and an additional 3500 tons would be required for disposal of the waste to be produced in their lifetime by the plants currently under operation.

Long-standing efforts have been made to determine experimentally the weathering of these glasses by aqueous solutions under subsurface conditions. As prediction of long-term stability involves extrapolations of the time scale of laboratory studies over a great many orders of magnitude, modeling of alteration reaction is a critical step. As a matter of fact, the Gibbs free energy difference between the glass and the relevant ions in aqueous solutions is the driving force of the alteration reaction. In other words, modeling of water-glass interactions should have a sounder basis if the Gibbs free energies of dissolution were better known.

These Gibbs free energies can be determined from the Gibbs free energies of formation of the glasses and

of the species dissolved in aqueous solutions. At least for reasonably dilute solutions, the latter can be accurately calculated as a function of temperature and solution composition.¹⁾ In contrast, the former can be obtained from available thermochemical data only for a few silicate glasses of geological interest. To obviate this problem, empirical models have been set up,²⁻⁴⁾ but it is difficult to ascertain their precision because of the very lack of experimental data with which they could be compared. To remedy this problem, we have thus determined experimentally a rather extensive set of Gibbs free energies of dissolution from which a number of thermochemical and structural implications have been drawn.

In this review, we first describe how Gibbs free energies of formation (from oxide components) can be determined for the complex borosilicates used in nuclear waste storage. We then review briefly the results obtained for simple glasses, and more complicated compositions as well, and compare these results with the values obtained from empirical models. In view of the special importance of ternary $\text{Na}_2\text{O-B}_2\text{O}_3\text{-SiO}_2$ glasses in a wide range of industrial contexts, we finally examine the structural information that can be gained for them from the new thermochemical data. For lack of space, we refer to

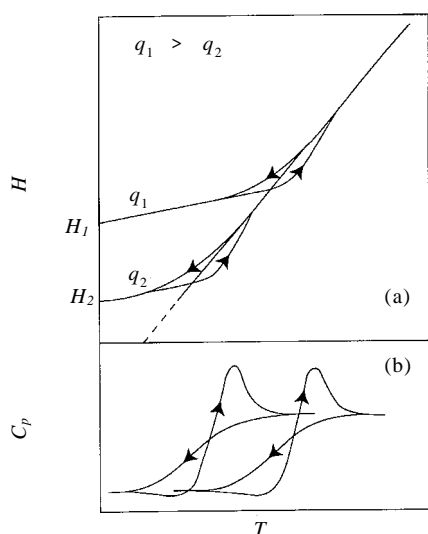


Fig.1 Heat capacity and enthalpy changes through the glass transition (from ref.6).

another contribution for application of these results to glass weathering and, in particular, to the important problem of the decrease with time of the alteration reaction rate.⁵⁾

2. Methodology

Thermochemistry of glasses

When dealing with glasses, one must first recall that these substances are not in internal equilibrium because their thermodynamic properties do not depend only on temperature and pressure, but also on thermal history. The glass transition thus is an irreversible phenomenon, as also shown by the fact that the existence of a heat capacity hysteresis (**Fig.1**) implies that some entropy is created when cycling through the transition range. For practical purposes, however, these complexities can be neglected and application of thermodynamics to glasses, *i.e.*, to substances with a fixed, disordered configuration, is operationally possible if account is properly taken of the influence of thermal history on the measured properties.

In practice, one can account for it by specifying the fictive temperature of the glass (\bar{T}), *i.e.*, the temperature at which the quenched configuration of the glass would be that of the equilibrium liquid (see ref.7). Although such a single order parameter is unlikely sufficient to characterize rigorously the state of an amorphous

substance, the practical justification for its use in this study is that the second-order thermodynamic properties of silicate glasses depend little on thermal history except at very low temperatures⁸⁾ or within the glass transition range. The differences in any thermophysical property between two glasses with fictive temperatures \bar{T}_1 and \bar{T}_2 can then be simply evaluated. The enthalpy and entropy differences are for instance

$$\Delta H = \int_{\bar{T}_1}^{\bar{T}_2} \Delta C_p dT, \quad \Delta S = \int_{\bar{T}_1}^{\bar{T}_2} \Delta C_p / T dT \quad (1)$$

where ΔC_p is the heat capacity difference between the liquid and glassy states.

Of course, the next question is how the fictive temperature of a glass is known. When a sample is annealed for a long time at the low end of the glass transition range, then the relaxation kinetics is slow and \bar{T} is equal to the annealing temperature. In case of continuous cooling, it is the glass transition temperature as defined by the intersection of the glass and liquid property of interest.

Gibbs free energies of formation

There exist a great many different methods to determine Gibbs free energies of formation. For oxide compounds, it is generally more convenient to determine separately the enthalpy and entropy parts of ΔG_f° with

$$\Delta G_f^\circ = \Delta H_f^\circ - T\Delta S_f^\circ \quad (2)$$

Specifically, the enthalpy of formation (ΔH_f°) is usually obtained from measurements of enthalpies of solution in an appropriate solvent

$$\Delta H_f^\circ = \sum n_i \Delta H_{si} - \Delta H_s \quad (3)$$

where ΔH_s is the enthalpy of solution of the glass, n_i the quantity in mole of oxide i present in one mole of glass, and ΔH_{si} the enthalpy of solution of oxide i . When the composition of the glass includes refractory oxides like CaO and MgO, dissolution in acid solutions (HF, for instance at temperatures close to ambient) is generally incomplete. For getting accurate results, dissolutions must therefore be made in oxide melts at temperatures near 700 (see ref.9).

As for the entropy of formation, it is obtained in the same way from the entropies of the glass (S) and those of the constituting oxides (S_i)

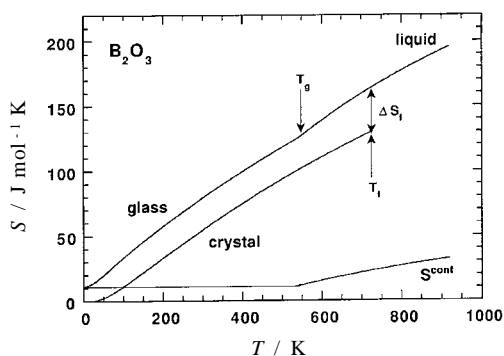


Fig.2 Residual entropy of B₂O₃ glass as derived from the entropy of fusion of the crystal and integration of the heat capacities in the crystalline, glassy and liquid states, and configurational entropy of the glass and liquid.¹⁰⁾

$$\Delta S_f \circ = \sum n_i \Delta S_i - \Delta S \quad (4)$$

For all these materials, the entropy can be expressed as

$$S(T) = S(T_0) + \int_{T_0}^T C_p / T dT \quad (5)$$

For a perfect crystal we have $S(T_0) = 0$ and the entropy of formation is

$$\Delta S_f \circ = S - \sum n_i S_i \quad (6)$$

As disordered substances, however, glasses do not obey the third law and have instead large residual entropies which represent the configurational entropy of the liquid that has been quenched at the glass transition

$$S(T_0) = S^{conf}(T_g) \quad (7)$$

This entropy can be determined through calorimetric measurements only in the special case of glasses which have the same composition as congruently melting crystals (**Fig.2**). For complex silicate glasses, the lack of a calorimetric method is compounded by the fact that $S(T_0)$ strongly depends on composition and can represent up to 30% of the total room-temperature entropy.¹⁰⁾ For borosilicates, this contribution is still more important, as will be shown below.

Configurational entropy

To obviate this problem, we have determined configurational entropies from viscosity measurements

as described in detail by Richet¹²⁾ for a variety of silicate melts. The starting point is the fact that viscous flow takes place through configurational changes in liquids. Viscosity (η) is low when these changes can occur independently in small regions of the liquid, *i.e.*, when the configurational entropy is large. On this basis, one derives from the theory of relaxation processes in viscous liquids set forth by Adam and Gibbs¹³⁾ that

$$\log \eta = A_e + B_e / TS^{conf} \quad (8)$$

where A_e is a pre-exponential term and B_e a constant proportional to the Gibbs free energy barriers hindering the cooperative rearrangements of the structure required for viscous flow. On the other hand, between T_g and any temperature T the configurational entropy increases as

$$S^{conf}(T) = S^{conf}(T_g) + \int_{T_g}^T C_p^{conf} / T dT \quad (9)$$

where C_p^{conf} is the configurational heat capacity. As long been justified for silicate melts,⁸⁾ it can be taken as

$$C_p^{conf}(T) = C_{pl}(T) - C_{pg}(T_g) \quad (10)$$

where $C_{pl}(T)$ is the heat capacity of the liquid at T , which was measured from T_g to more than 1500 K (Linard, unpublished data), and $C_{pg}(T_g)$ that of the glass at the glass transition temperature. Note that one of the reasons why this approximation is appropriate for silicate melts is that the glass transition always takes place when the heat capacity of the glass is close to the Dulong and Petit limit.

When $S^{conf}(T_g)$ is known from calorimetric measurements, eqns⁸⁻¹⁰⁾ constitute a two-parameter expression which reproduces quantitatively the viscosity observations over more than 13 orders of magnitude for silicate melts.^{8,13)} Alternatively, one can consider eqns⁸⁻¹⁰⁾ as a 3-parameter expression with which $S^{conf}(T_g)$ is fitted to the viscosity measurements. When possible, comparisons between both kinds of determinations of $S^{conf}(T_g)$ indicate very good agreement (**Fig.3**). This is the justification for using the combination of viscosity and calorimetry data embodied by eqns⁸⁻¹⁰⁾ to determine configurational entropies of silicate melts. This method has two main advantages.¹⁰⁾ First, it is applicable to any melt, how complex its composition may be. Second, the configurational entropies at T_g determined in this

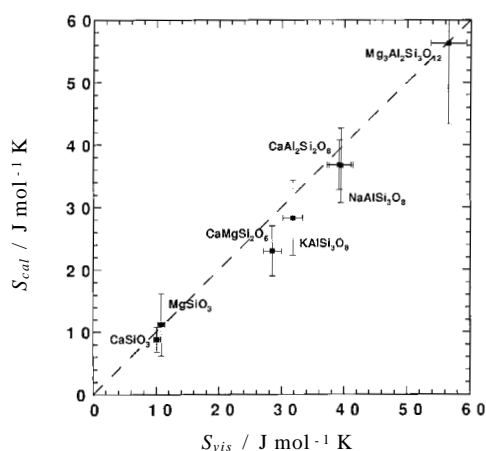


Fig.3 Comparison between configurational entropies frozen in at T_g determined from calorimetry (S_{cal}) and viscometry (S_{vis}). Data from ref.10.

way are accurate to within 5 % and are thus more accurate than the calorimetric determinations, which represent small differences between large numbers.

3. Results

Although silica-rich borosilicate glasses have long found a wide range of applications, their thermochemical properties have been little investigated. Solution calorimetry¹⁴⁾ and heat capacity¹⁵⁾ measurements are exceptions in this respect. Since nuclear waste storage glasses are based on sodium borosilicates, we have paid particular attention to the silica rich portion of the ternary system $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$. Including available data for sodium silicate glasses,⁷⁾ we have thus considered a total of 9 glasses in this system. Two compositions (AVM and SON) have a special importance, for they represent the projection in this ternary system of the two series of glasses actually used in France for nuclear waste storage. To determine the effects of the numerous oxides present in these glasses on Gibbs free energies, we have added other oxides in the order of their abundances, namely, Al_2O_3 , CaO , ZrO_2 , Ce_2O_3 , Li_2O , by keeping the $\text{SiO}_2:\text{Na}_2\text{O}:\text{B}_2\text{O}_3$ ratios constant and equal to those of SON-3. As examples, we list in **Table 1** the compositions of some of the glasses investigated.

The calorimetry and viscosity results are summarized in **Table 2**. Since the measurements required to evaluate eqn (1) must be performed from the vicinity of 0 K to

Table 1 Chemical composition (wt %), gram formula weight (gfw) and number of atoms of glasses per gfw (n).

	SON-3	AVM-3	BSN-5/16	BSN-11/32	SON	AVM
SiO_2	67.58	57.36	78.45	56.60	52.46	45.28
B_2O_3	18.27	19.63	5.70	10.96	13.96	16.28
Na_2O	14.12	22.94	15.81	32.39	11.03	18.29
Al_2O_3	0.02	0.06	0.01	0.00	3.34	6.67
CaO					4.99	0.98
MgO						8.50
ZrO_2					1.49	0.53
Ce_2O_3					0.20	0.13
Li_2O					4.59	0.46
Others ^a	0.02	0.02	0.03	0.05	7.94	2.88
gfw (g)	62.117	62.429	60.955	61.766	69.220	67.828
n	3.3662	3.3940	3.1147	3.2198	3.3147	3.3820

^a Include Fe_2O_3 , ZnO , MoO_3 , Cs_2O , Nd_2O_3 , La_2O_3 , ThO_2 , NiO , Cr_2O_3 , P_2O_5 , UO_2 , SrO , Y_2O_3 , MnO , CoO , etc.

Table 2 Relative entropies ($\text{J mol}^{-1} \text{K}^{-1}$), coefficients of C_p equations ($\text{J mol}^{-1} \text{K}^{-1}$) for glasses (g) and liquids (l), enthalpies of formation determined from enthalpies of solution in lead borate at 970 K (kJ mol^{-1}) and coefficients of the equations (7) for the viscosities (log Pa.s).

	SON-3	AVM-3	BSN-5/16	BSN-11/32	SON	AVM
$S_{298}-S_0$	48.81	52.69	49.70	56.00	52.25	54.97
a_g	139.36	121.28	92.838	125.14	53.765	41.117
$10^3 b_g$	-2.903	4.149	8.055	1.621	37.332	40.500
$10^{-5} c_g$	5.799	1.553	-2.329	2.582	-11.613	-17.203
d_g	-1641.1	-1236.8	-749.62	-1285.7	0	365.96
$C_{pg}(T_g)$	82.63	82.45	72.96	79.96	82.53	84.39
a_l	107.49	100.41	96.33	104.36	108.91	101.61
b_l	0	4.112	0.359	0	-2.4822	-0.6125
$10^{-5} c_l$	0	121.04	-62.155	51.632	71.774	141.54
ΔH_f°	-41.69	-56.00	-35.98	-61.40	-23.58	-38.86
A_e	-1.555	-2.667	-0.607	-1.924	-1.336	-2.017
$10^{-5} B_e$	1.328	1.916	1.022	1.410	1.310	1.763
$S^{conf}(T_g)$	11.73	16.03	9.14	12.58	13.18	16.71
T_g	895.0	844.7	821.7	752.7	817.1	815.9

elevated temperatures, it is important to make sure that the various kinds of heat capacity determinations performed are consistent. In our work (**Fig.4**), this has been achieved through a combination of adiabatic^{16,17)} and DSC (differential scanning calorimetry)¹⁸⁾ C_p

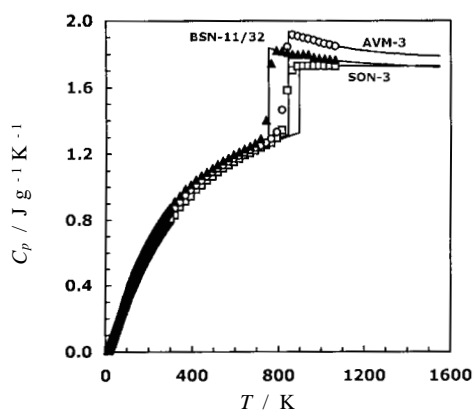


Fig.4 Heat capacities of selected sodium borosilicate glasses and liquids as determined from adiabatic, DSC and drop-calorimetry experiments. Experimental data and fitted values as given by eqn (11).

measurements for the glasses and, for liquids, through a combination of DSC and relative enthalpy experiments made with the drop method in an ice calorimeter.¹⁹⁾

The relative entropies S_{298-S_0} listed in **Table 2** have been derived from integrations of the adiabatic C_p measurements. For the glasses and liquids, fits have been made to the C_p and $H_T - H_{273}$ data with equation of the form

$$C_p = a + bT + c/T^2 + d/T^{0.5} \quad (11)$$

The solution calorimetry experiments have been made with lead borate solutions at 970 K.²⁰⁾ They refer to supercooled liquids since this temperature is higher than the glass transition temperatures of all materials. They show good agreement with the previous results.¹⁴⁾ Finally, viscosities have been measured between $10^{8.7}$ and $10^{13.1}$ Pa.s with a creep apparatus,²¹⁾ and between 1 and $10^{4.8}$ Pa.s with the Couette-type apparatus used in previous investigations.²²⁾ The results are plotted in **Fig.5** for the compositions dealt with in **Fig.4**. The fit parameters of eqn (8) to the measurements are also included in **Table 2**.

The Gibbs free energies of formation determined from the results of **Table 2** are listed in **Table 3** for fictive temperatures arbitrarily taken equal to the drop-calorimetry glass transition temperatures of **Table 2**. We finally calculated Gibbs free energies of dissolution in aqueous solutions. For this purpose we assumed for the oxides the dissolution reactions listed in **Table 4**, for

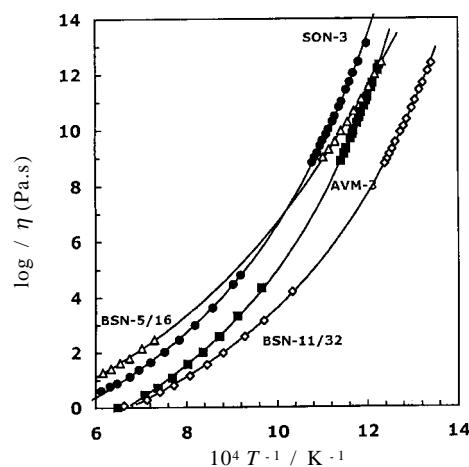


Fig.5 Viscosity against temperature for the materials of Fig.1. Note that the liquids with the steepest viscosity slopes in this Arrhenius diagram have the highest configurational heat capacities.

Table 3 Gibbs free energies of formation (ΔG_f°) and experimental (exp) and calculated (calc) Gibbs free energies of dissolution (ΔG_d°) of the glasses at 25 °C (kJ mol⁻¹).

	SON-3	AVM-3	BSN-5/16	BSN-11/32	SON	AVM
ΔG_f°	-45.30	-61.09	-39.36	-65.82	-28.42	-45.76
$\Delta n_i \Delta G_d^\circ$	-50.47	-86.01	-51.23	-119.36	-55.56	-72.09
$\Delta G_d^{\circ \text{exp}}$	-5.17	-24.92	-11.87	-53.55	-27.14	-26.33
$\Delta G_d^{\circ \text{calc}^a}$	-55.12	-89.97	-56.65	-123.27	-59.18	-75.21
$\Delta G_d^{\circ \text{calc}^b}$	-18.34	-32.78	-19.85	-53.03		

^a Paul (1977)

^b Conradt (1999), see text.

which we used the Gibbs free energies of reaction listed by Woods and Garrels.²³⁾

The Gibbs free energy of dissolution are compared in **Table 2** with the values predicted from empirical models of calculation for similar dissolution reactions. The first model proposed by Paul²⁾ assumes that the Gibbs free energies of dissolution of glasses in water are approximately an additive function of those of vitreous silica and the endmember oxide compounds. In fact, it yields poor agreement with our experimental data (**Table 3**) because it fails to account for two fundamental features of the vitreous state, namely, the significant enthalpies

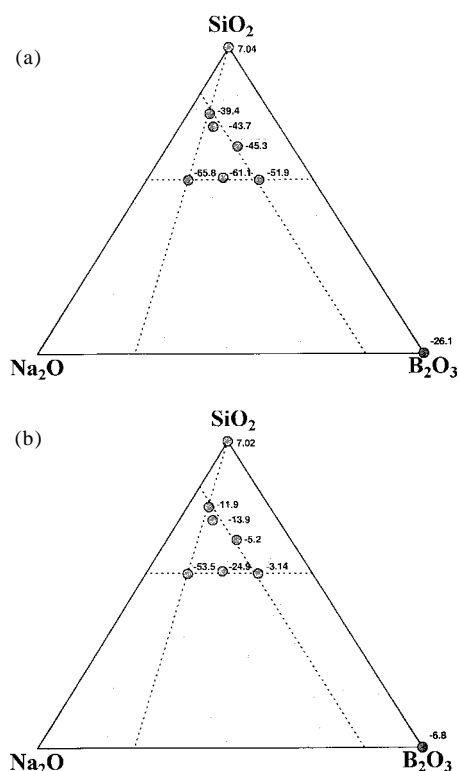
Table 4 The Gibbs free energies used of dissolution for endmember oxides.

Dissolution reaction		ΔG_d°
$\text{SiO}_2 + 2\text{H}_2\text{O}$	H_4SiO_4^0	14.06
$\text{B}_2\text{O}_3 + 3\text{H}_2\text{O}$	$2\text{B}(\text{OH})_3$	- 32.90
$\text{Al}_2\text{O}_3 + 5\text{H}_2\text{O}$	$2\text{Al}(\text{OH})_4^- + 2\text{H}^+$	155.79
$\text{Na}_2\text{O} + 2\text{H}^+$	$2\text{Na}^+ + \text{H}_2\text{O}$	- 381.96
$\text{CaO} + 2\text{H}^+$	$\text{Ca}^{2+} + \text{H}_2\text{O}$	- 186.77
$\text{Li}_2\text{O} + 2\text{H}^+$	$2\text{Li}^+ + \text{H}_2\text{O}$	- 261.78
$\text{K}_2\text{O} + 2\text{H}^+$	$2\text{K}^+ + \text{H}_2\text{O}$	- 481.64
$\text{ZrO}_2 + 4\text{H}^+$	$\text{Zr}^{4+} + 2\text{H}_2\text{O}$	32.40
$\text{Ce}_2\text{O}_3 + 6\text{H}^+$	$2\text{Ce}^{3+} + 3\text{H}_2\text{O}$	- 266.50

of mixing between such components and the existence of configurational entropy in silicate, aluminosilicate and borosilicate glasses. In the recent model of Conradt,⁴⁾ these features are in contrast incorporated through the use of vitreous components such as SiO_2 , Na_2SiO_3 , B_2O_3 , etc., for which complete thermochemical information is available. Because there are several ways of expressing the composition of our glasses in terms of this set of components, the calculated Gibbs free energies of solution are not unique. In **Table 3** we have listed the values that are in closest agreement with the experimental data, which have been obtained with SiO_2 , Na_2SiO_3 , $\text{Na}_2\text{Si}_2\text{O}_5$, B_2O_3 and $\text{Na}_2\text{B}_8\text{O}_{13}$ components. The considerable improvement with respect to Paul's model is obvious. The differences can remain significant, however, and use of ternary components closer in composition to the glasses of interest than the binary silicates and borates used should ensure a better precision.

4. Discussion

The first effect to be discussed is that of thermal history on the energetics of glasses. We will take the SON-3 sample as an example (referred to as BSN-14/18 in ref.18). By analogy with the relaxation experiments performed on other borosilicates,²²⁾ we estimate that the lowest fictive temperature that could be achieved after isothermal annealing for a few days would be 827 K, which is the temperature at which the viscosity would be $10^{13.5}$ Pa.s. The Gibbs free energy of formation of such a glass would be $-46.4 \text{ kJ mol}^{-1}$ and thus be 1.1 kJ mol^{-1} lower than that of the glass with $\bar{T} = 895 \text{ K}$ formed in drop-calorimetry experiments (**Table 3**). We

**Fig.6** Gibbs free energies of formation (a) and dissolution (b) of ternary sodium borosilicates.

thus conclude that annealing should improve slightly the resistance of glasses to alteration.

The enthalpies of solution of the investigated glasses in the system $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ range from -0.24 to 0.39 kJ mol^{-1} . From these results, we find that the enthalpies of mixing between SiO_2 glass and the relevant alkali borate glasses are negative along the join for which $\text{Na}_2\text{O}/\text{B}_2\text{O}_3 = 3$. These conclusions are in agreement with previous work¹⁴⁾ and consistent with available data on the binary joins $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ and $\text{Na}_2\text{O}-\text{SiO}_2$. This negative enthalpy of mixing implies association of borate and silicate groups in the glass structure. At higher boron content and 56.6 mol % SiO_2 , the enthalpy of mixing increases from -6.5 kJ mol^{-1} for the SON-3 sample to $+2.6 \text{ kJ mol}^{-1}$ for BSN-29/14. This is in agreement with the presence of metastable immiscibility in glasses at higher silica content which should give rise to positive enthalpies of mixing.

Boron is essentially three coordinated by oxygen atoms in pure B_2O_3 , whereas it exists in three- (^{III}B) and

four- (^{IV}B) fold coordination in sodiumborosilicates.^{26,27)} From solution calorimetry measurements (ref.14 and **Table 2**), we observe that enthalpies of mixing decrease when the proportion of Si-O-^{IV}B bonds increases. This trend appears to parallel the increase of the Gibbs free energy of formation of glasses when the proportion of Si-O-B bonds increases. This is another way of saying that a purely tetrahedral glass framework of Si and only ^{IV}B would be more resistant to leaching than networks in which BO₃ triangles are also incorporated.

The composition dependence of Gibbs free energies in the ternary system Na₂O-B₂O₃-SiO₂ is represented in **Fig.6**. These Gibbs free energies decrease with decreasing silica content. The decrease is stronger for high Na₂O/B₂O₃ ratios. At a constant silica content of 56.7 mol %, for instance, ΔG_f° varies from -65.8 to -51.9 kJ mol⁻¹ for Na₂O/B₂O₃ = 3 and 0.5, respectively, whereas the value for vitreous silica is 7.04 kJ mol⁻¹. In the investigated high-silica part of the ternary system, a minimum energy seems to exist at low SiO₂ and high Na₂O contents. At a constant Na₂O content, ΔG_f° varies almost linearly. This general linear decrease could be explained by the energy difference between silicate and borate networks and by the low mixing enthalpies along the binary SiO₂-B₂O₃ join¹⁴⁾ which is compensated by the high mixing entropies observed in this study (see below) when alkali cations are present.

The effects of added oxides on these Gibbs free energies for the SON series are shown in **Fig.7** where the SiO₂ mole fraction has been used as the composition variable. The base glass SON-3 has the lowest Gibbs free energy of formation. Addition of the other oxides leads to increases of ΔG_f° by more than 20 kJ mol⁻¹ in the same regular order in which the sodium borosilicate matrix is diluted with other oxides. Correlatively, the magnitude of the Gibbs free energy of dissolution increases in the same order but with much less regularity due to the specificity of the energetics of ion formation in aqueous solutions. For instance, addition of 4.1 mol % Al₂O₃ to the SON-3 base glass results in a 7 kJ mol⁻¹ increase of ΔG_d° whereas further addition of 6.3 mol % CaO translates into a 12.4 kJ mol⁻¹ decrease of ΔG_d° .

When discussing the thermodynamic stability of glasses with respect to aqueous solutions, one should keep in mind that the Gibbs free energies of dissolution markedly depend on pH. In **Fig.7(b)**, for instance, all

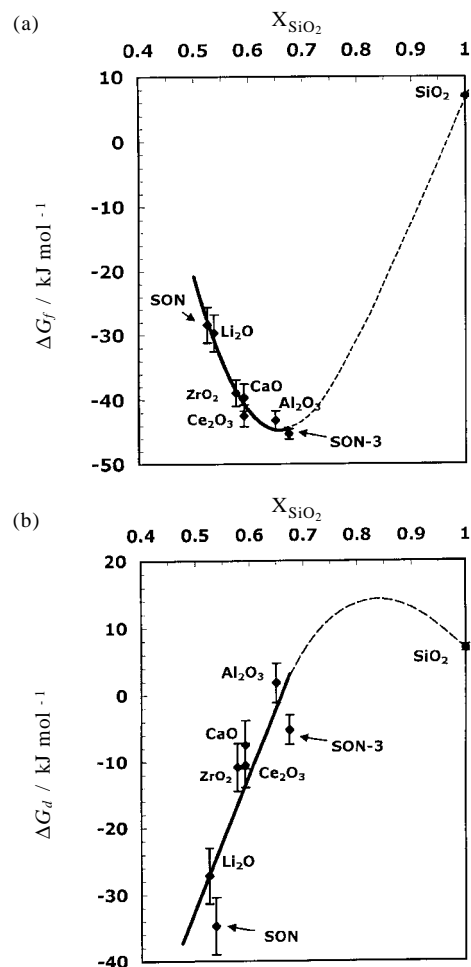


Fig.7 Influence of other oxides added to the SON-3 base sodium borosilicate on the Gibbs free energies of formation (a) and dissolution (b) as plotted against the SiO₂ content. The dashed lines are a guesstimated extrapolations to pure SiO₂.

Gibbs free energies of dissolution are obtained for infinitely diluted H₄SiO₄ solutions which are not relevant under natural conditions. Hence, the positive Gibbs free energies of dissolution of pure SiO₂ and SiO₂-rich glasses shown in **Fig.7(b)** should not suggest that these materials are best suited for waste storage since they would not dissolve in pure water. These effects will be discussed in a forthcoming publication. In the following, we will just compare the effects of composition changes within the ternary system Na₂O-B₂O₃-SiO₂ to those of the other oxides. One then arrives at the important conclusion that both are of similar magnitude on Gibbs

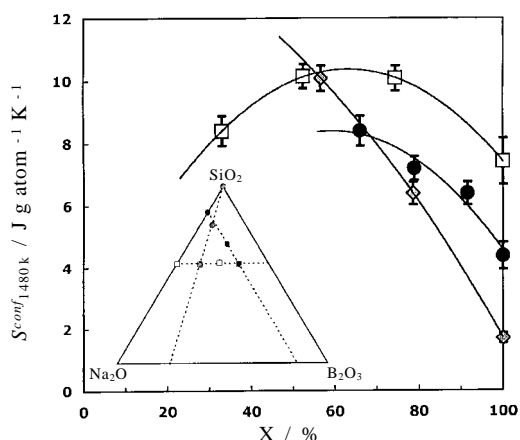


Fig.8 Configurational entropy at 1450 K along the three different binary joins shown.

free energies. As far as the energetics of dissolution are concerned, this indicates that the alteration kinetics could be different for simple, model glasses and for the complex glasses actually used for nuclear storage. This problem will also be discussed in more detail in a subsequent paper.

Independently of any concern for glass stability, note that our results lead to structural inferences of more general interest. At low temperatures, for instance, the heat capacity of silicate glasses has been shown to be a sensitive probe of short- and medium-range order.^{24,25)} This sensitivity manifests itself below 200 K by marked deviations of C_p from additivity with respect to the oxide components.¹⁷⁾ This nonideality is mostly due to the coordination differences between pure B_2O_3 and sodium borosilicates. In SON-3, for instance, ^{10}B and ^{11}B should be in a 27:73 ratio²⁷⁾ and it is in fact possible to determine from the calorimetric results partial molar heat capacities and entropies for both coordination states in B_2O_3 components.¹⁷⁾ The values derived for $^{11}B_2O_3$ happen to be similar to those for pure B_2O_3 . As the existence of the so-called boroxol rings (*e.g.*, planar, three-membered rings of BO_3 units) exerts a profound influence on the entropy of pure B_2O_3 ,¹¹⁾ this indicates that boroxol rings are also present in borosilicate glasses.

Finally, a few words are in order about configurational entropies. On a g atom basis, the entropies of the glasses of **Table 2** at the glass transition temperature range between 2.9 and 4.9 $J g atom^{-1} K^{-1}$. This interval is much higher than the 1.6 ~ 3.2 $J g atom^{-1}$

K^{-1} range reported for silicates and aluminosilicates²⁸⁾ and is within the 3.1 ~ 4.6 $J g atom^{-1} K^{-1}$ range found for the three borosilicates previously studied.²⁾ As already discussed,¹⁸⁾ this likely results from the existence of the aforementioned distinct boron species.

Our new results allow more detailed conclusions to be drawn in this respect. To eliminate any bias resulting from different glass transition temperatures, we have plotted in **Fig.8** configurational entropies for the same temperature of 1480 K along the three binary joins delineated by the samples investigated. Either at constant Na_2O/B_2O_3 ratio or at constant B_2O_3 content, S^{conf} decreases markedly when the SiO_2 content increases. As will be described elsewhere, this is an effect of the complex speciation of boron. Mixing of these species results in an increase of configurational entropy, whose magnitude increases with the boron content. At constant SiO_2 content, in contrast, S^{conf} goes through a maximum when the Na_2O and B_2O_3 contents are similar. From the binary system Na_2O-SiO_2 to this maximum, the increase of S^{conf} is of course due to the same reason, whereas the subsequent decrease originates in the presence of only ^{11}B in glasses of the other limiting binary join $B_2O_3-SiO_2$.²⁸⁾

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